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| 著者 | Kyono Atsushi |
| journal or publication title | Physics and chemistry of minerals |
| volume | 40 |
| number | 9 |
| page range | 717-731 |
| year | 2013-10 |
| 権利 | (C) Springer-Verlag Berlin Heidelberg 2013 The final publication is available at Springer via http://dx.doi.org/10.1007/s00269-013-0607-3 |
| URL | http://hdl.handle.net/2241/00124751 |

doi: 10.1007/s00269-013-0607-3

**Ab initio quantum chemical investigation of arsenic sulfide molecular
diversity from As₄S₆ and As₄**

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ABSTRACT

The structural diversity of arsenic sulfide molecules in compositions between As_4S_6 and As_4 was investigated using ab initio quantum chemical calculations. The As_4S_6 molecule consists of four trigonal pyramid coordinations of As atoms bonding to three S atoms. In the As_4S_5 composition, only one type of molecular configuration corresponds to an uzonite-type molecule. In the As_4S_4 composition, two molecular configurations exist with realgar-type and pararealgar-type molecules. Three molecular configurations are in the As_4S_3 composition. The first configuration comprises trigonal pyramidal As atom coordinations of two types: bonding to two S atoms and one As atom, and bonding to one S atom and two As atoms. The second is the molecular configuration of dimorphite. The third comprises trigonal pyramidal As atom coordinations of two types: bonding to three As atoms, and bonding to one As atom and two S atoms. The As_4S_2 composition allows molecular configurations of two types. One is comprised of trigonal pyramidal As atom coordinations of one type bonding to two As atoms and one S atom. The other comprises trigonal pyramidal As atom coordinations of three types: bonding to two S atoms and one As atom, bonding to one S atom and two As atoms, and bonding to three As atoms. The As_4S molecule has trigonal pyramidal As atom coordinations of two types: bonding one S atom and two As atoms, and bonding to three As atoms. The As_4S composition permits only one molecular configuration, which suggests that the mineral duranusite comprises the As_4S molecular geometry. In all, ten molecular

configurations are predicted in the molecular hierarchy of the arsenic sulfide binary system. The simulated Raman spectral profiles are helpful in searching for undiscovered arsenic sulfide minerals.

Keywords: arsenic sulfide minerals, molecular configuration, diversity, hierarchy, ab initio quantum chemical calculation

INTRODUCTION

Arsenic sulfide minerals are found primarily in active volcanic areas as sublimate products and in low-temperature hydrothermal sulfide veins as minor constituents. They are also found in lead, silver, or gold ore deposits associated with other As–Sb sulfides such as getchellite or wakabayashilite. The arsenic sulfide minerals known to date are duranusite As_4S , dimorphite As_4S_3 , realgar and pararealgar As_4S_4 , non-stoichiometric $\text{As}_4\text{S}_{4+x}$ ($0 < x < 0.5$), alacranite As_8S_9 , uzonite As_4S_5 , and orpiment As_2S_3 . Most of the arsenic sulfide minerals have typical molecular structures with cage-like molecules held together by weak interactions of van der Waals forces. In the binary system of arsenic sulfide minerals, molecular configurations of four types have been reported to date (Bonazzi and Bindi, 2008). The dimorphite-type molecule comprising four As and three S atoms (Whitfield 1970; 1973a), realgar-type molecule composed of four As and four S atoms (Mullen and Nowacki 1972; Porter and Sheldrick 1972), a pararealgar-type molecule with a different molecular configuration from that of realgar (Bonazzi et al. 1995; Kutoglu 1976), and uzonite-type molecule constructed from four As and five S atoms (Whitfield 1973b; Bindi et al. 2003). The structures of non-stoichiometric $\text{As}_4\text{S}_{4+x}$ and alacranite As_8S_9 with atomic ratio As:S = 4:4.5 consist of a mixed packing of realgar-type and uzonite-type molecules (Bonazzi et al. 2003). The uzonite-type molecule can be found in wakabayashilite $[(\text{As,Sb})_6\text{S}_9][\text{As}_4\text{S}_5]$ as well (Bonazzi et al. 2005). Of them, only orpiment exhibits a corrugated layered structural arrangement (Mullen and Nowacki 1972). The

crystal structure of duranusite As_4S (e.g., Johan et al. 1973; Marquez-Zavalia et al., 1999; Mladenova, 2000), however, remains undetermined.

An As atom is well known to form a typical one-sided three-fold (trigonal) coordination because of the presence of the $4s^2$ stereochemically active lone pair. The coordination geometry has three pyramidal bonds and a lone electron pair occupying the fourth arm of a tetrahedron. In all As–S binary minerals from dimorphite As_4S_3 to orpiment As_2S_3 , the trigonal pyramidal coordinations of an As atom are classifiable into three types: an As atom is bonded to (1) three S atoms, (2) two S atoms and one As atom, and (3) one S atom and two As atoms. The arsenic sulfide minerals show an extremely wide range of As:S atomic ratio from 4:1 to 4:6 with a large geometric change. In addition, a different pyramidal bond combination among the three types can be considered such like a relationship between orpiment and anorpiment (Kampf et al 2011). It is well known, moreover, that identifying arsenic sulfide minerals is considerably difficult because they are often of low abundance and are very fine-grained. Atomic and electronic structures, physical and chemical properties can be modified with decreasing the particle size to nanoscale. The finely particles (nanoparticles) of arsenic sulfides composed of not only crystalline but amorphous should have different properties to bulk material. Therefore, a high probability exists that a new molecular configuration or a novel bonding will be found in the As–S system.

The primary purpose of this study is to predict how many molecules can exist in the As–S

system and what geometries the molecules can possess. Moreover, this report presents a hierarchical diagram of arsenic sulfide molecules based on their structural diversity. To achieve the goals, ab initio quantum chemical calculations were performed for all possible As–S molecular geometries. The presented results will enable us to consider numerous mineralogical implications.

METHODS

All calculations of optimized geometry, total energy, charge distribution of atoms (Mulliken electron population analysis), molecular orbital, HOMO–LUMO energy gap, and Raman spectra were conducted using the quantum chemical calculation software package Gaussian-09 (Frisch et al. 2009). The Raman intensities related to polarizability derivatives are calculated based on Frisch et al (1986). To apply the most appropriate calculation method to optimize the molecular geometries, preliminary calculations were performed using three ab initio quantum chemical methods (B3LYP density functional theory; DFT, Hartree–Fock; HF, and second-order Møller–Plesset perturbation theory; MP2) and four different basis sets (6-31G(d), 6-31+G(d), 6-311G(d), and 6-311+G(d)) on the four molecules, which are dimorphite, realgar, pararealgar, and uzonite. Table 1 presents results comparing molecular geometries between simulations and observations. Results show that the HF and MP2 methods gave the closest molecular geometry to those actually measured using X-ray diffraction analysis. Taking the results of Mulliken population analysis into consideration, moreover,

the results with the HF calculation is the best fit for the all arsenic sulfide molecules. In the study, therefore, all calculations were performed at the HF level using the 6-311G(d) basis set. The overall charges on molecules and spin multiplicities were, respectively, set as neutral and singlet. To build the As–S molecular hierarchy diagram, an As₄S₅ molecule (Bindi et al. 2003), which is the largest molecule ever known to exist in the As–S binary system, was used as a starting molecule for calculations. The final atomic positions obtained with the structural optimization calculations are reported in Table 2. The origin in the Cartesian coordinate system is calculated to coincide with the center of gravity of a molecule. All bond lengths and bond angles are given in Table 3.

RESULTS AND DISCUSSION

As₄S₅ molecule

Figure 1 displays the optimized molecular geometry and bond lengths of the As₄S₅ molecule. The molecule comprises trigonal pyramidal As atom coordinations of two types: the As₃ and As₄ are bonded to three S atoms, and the As₁ and As₂ are bonded to two S atoms and one As atom (Fig. 1). The average As–S bond length of 2.246 (6) Å is fairly close to the value of 2.248 (9) Å measured using the XRD method (Bindi et al. 2003). The bond angles in the trigonal pyramid with three S atoms are, respectively, 98.1, 105.7, and 105.7 °. Those with two S atoms and one As atom are, respectively, 101.2, 101.2, and 102.9 °. The As₃ and As₄ with three S atoms carry higher positive

charge than the As1 and As2 with two S atoms and one As atom (Table 4). The S5 bonded to the As3 and As4 has higher negative charge than the other S atoms (Table 4). Because of the higher negative charge of the S5, the As3-S5, and As4-S5 bond lengths of 2.258 Å become longer than the other As-S bonds. In addition, all bond angles coordinated with the S5, not only As3-S5-As4 but S1-As4-S5, S2-As4-S5, S3-As3-S5, S4-As3-S5, are larger than the other As-S-As and S-As-S angles. Particularly, the As3-S5-As4 bond angle of 117.5° is the largest among the entire calculated arsenic sulfide molecules examined in this study (Table 3). The same geometrical feature has been observed in the As₄S₅ uzonite molecule (Bindi et al. 2003). Consequently, an estimated dipole moment shows 0.953 D (Table 4), which is similar to that of a H₂S molecule (0.97 D) (Nelson et al. 1967).

As₄S₆ molecule

The coordination environment of an As atom can allow the As₄S₅ molecule to possess a S atom between the As1 and the As2 (Fig. 1) because the three pyramidal bonds change from two As-S and one As-As into three As-S. Therefore, the geometry of an As₄S₆ molecule was formed by adding a S atom between the As1 and As2 in the As₄S₅ molecule. It was used for an initial model of the structural optimization calculation. Figure 2 presents the optimized As₄S₆ molecular geometry and the bond length distribution. The resulting molecule consists of only one trigonal pyramidal coordination type: the As atom is bonded to three S atoms. The coordination configurations of the As atoms exhibit a distinctly trigonal pyramidal arrangement with the averaged As-S bond length of

2.2471 (3) Å and the average S–As–S bond angle of 105.91 (2) ° (Table 3). The average As–S–As bond angle of the bridged S atoms is 116.20 (1) °. Little variation exists in the bond lengths and angles in the As₄S₆ molecule. Atomic charge is distributed equally between the As and S atoms (Table 4). This fairly symmetrical arrangement forms a fully isotropic molecular geometry of the As₄S₆ with an extremely small electric dipole moment (0.007 D). The As₄S₆ comprises a cage-like molecule, whereas the structure of orpiment As₂S₃ with the same atomic ratio of the As₄S₆ molecule is comprised of chains of the trigonal pyramidal coordinations connected by bridged S atoms and cross-linked by van der Waals forces to form a corrugated layered structure (Mullen and Nowacki, 1972). The measured As–S bond lengths are 2.243 (5) – 2.308 (5) Å. The averaged As–S bond length is 2.28 (2) Å, which is slightly longer than the estimated As–S bond lengths in the As₄S₆ molecule. The most significant difference in the coordination environment is found in S–As–S bond angles. Compared with the As₄S₆ molecule, the S–As–S bond angles vary widely from 92.8 (2) to 105.0 (2) ° in orpiment. The As₄S₆ molecular geometry with the largest potential energy can exist as a molecule, but it might spontaneously decomposes into orpiment As₂S₃ consisting of the trigonal AsS₃ pyramids.

As₄S₄ molecules

Considering the hierarchy of the arsenic sulfide molecules, it is important to consider what geometries can derive from larger molecules. A molecular model in which the S5 is removed from

the As_4S_5 molecule (Fig. 1) was first optimized. The resulting optimized geometry and the bond length distribution are shown in Fig. 3a. The molecular configuration corresponds to that of realgar. The realgar-type molecule comprises only one type of trigonal pyramidal coordination: the As atom is bonded to two S atoms and one As atom. The averaged As–As and As–S bond lengths are, respectively, 2.5572 (2) and 2.2403 (0) Å. These are almost consistent with the observed As–As bond length of 2.5705 (7) Å and As–S bond length of 2.240 (7) Å in the realgar (Kyono et al. 2005). The As–As bond length of 2.557 Å is the longest among all of the calculated As–As bond arsenic sulfide molecules used in this study (Table 3). The averaged S–As–S, As–As–S, and As–S–As bond angles are, respectively, 95.14 (2), 99.64 (0), and 100.37 (0) °. These resemble those measured actually in realgar (94.8 (3), 99.5 (4), and 101.1 (3) °, respectively). No variation exists in the simulated bond lengths and angles. As a result of the isotropic molecular geometry, the positive and negative atomic charges are distributed equally between As and S atoms in the molecule (Table 4). The result shows agreement with the atomic charge calculated using DFT method (Bullen et al. 2003). Consequently, the As_4S_4 molecule possesses an almost zero dipole moment (Table 2).

Next, an initial molecular configuration for the optimization was formed with removal of the S4 from the As_4S_5 molecule (Fig. 1). Results of the detachment of an S atom except the S5 atom in the As_4S_5 molecule engender an equivalent As_4S_4 molecular geometry. The resulting molecular configuration and bond lengths are given in Fig. 3b. The molecule is exactly identical to that of

pararealgar (Bonazzi et al. 1995). The pararealgar-type molecule holds coordination environments of an As atom of three types: the As4 is bonded to three S atoms, the As2 and As3 are to two S atoms and one As atom, and the As1 is to one S atom and two As atoms (Fig. 3b). Contrary to the realgar-type, 0.05 Å variation in the As–S bond lengths is observed in the pararealgar-type molecule (Table 3). In the observed As–S bond lengths, wide variation exists from 2.190 (9) to 2.261 (8) Å as well (Bonazzi et al. 1995). In addition, the As1-S2 bond of 2.2155 Å is shorter than any other bond length among all calculated arsenic sulfide molecules in the study (Table 3). The shortest As–S bond is strictly consistent with that in the observed pararealgar-type molecule (Bonazzi et al. 1995). Bond angles in the trigonal pyramid with three S atoms are, respectively, 98.9, 98.9, and 104.4 °. Those with two S atoms and one As atom are, respectively, 86.0, 100.5, and 104.6 °. Those with one S atom and two As atoms are, respectively, 84.5, 101.8, and 101.0 °. It is important to note that a bond angle in a trigonal pyramid decreases concomitantly with increasing As atom in the trigonal pyramidal coordination. Furthermore, the As atomic charge decreases concomitantly with increasing As atom in the trigonal coordination. As a result of change of coordinated atoms, the As4 carries the highest positive charge, whereas As1 has the lowest positive charge within the molecule (Table 4). The result coincides exactly with that of the DFT calculation (Bullen et al. 2003). Furthermore, S3 with the highest negative charge forms the longest As–S bond with the As2 and As3. This geometrical tendency concurs with that in the As₄S₅ molecule. Regarding the As–S–As angles, the As2-S3–As3

bond angle shows the smallest angle among pararealgar-type molecules. With highly asymmetrical distribution of the atomic charges, the molecule holds a higher dipole moment (Table 4).

Light-induced phase transition from realgar to pararealgar

Figure 4 presents the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the As_4S_4 realgar-type molecule. Banerjee et al. (2003) fully described the bonding characteristics and electron distributions of all occupied valence molecular orbitals in the realgar-type molecule, except for the unoccupied valence molecular orbitals. The spatial distribution of the HOMO (Fig. 4a) shows strict correspondence with that obtained by Banerjee et al. (2003). In that study, it was proved that LUMO possesses a π -bonding character on the As1–As2 bond and over the S–As–S bonds (Fig. 4b). It is especially important to note, however, that a strong antibonding character exists between As3 and As4. We proposed a model of the light-induced phase transformation process by which the realgar-type molecule temporarily transforms to the As_4S_5 molecule with incorporation of an S atom between the As atoms (Kyono et al., 2005). The X-ray diffraction analyses additionally provided direct atomic resolution evidence of the formation of intermediate As_4S_5 phase in which half of the realgar molecule is retained in its envelope-type conformation (Naumov et al. 2007, 2010). Moreover, in the molecular orbital calculation, the energy band gap separating the HOMO and LUMO is 2.509 eV, which corresponds to wavelength of 494.2 nm. The realgar transforms into pararealgar at wavelengths between about 500 and 670 nm

(Douglass et al. 1992). Therefore, the excitation energy is approximately consistent with the wavelength at which the phase transformation occurs. Consequently, As–As bonding with the antibonding orbital would be broken under excitation conditions.

As₄S₃ molecules

First, a molecule model for geometry optimization was formed by removing S2 from the realgar-type molecule (Fig. 3a). Geometry optimization using an initial model that a S atom removed from the realgar-type molecule consequently reached an equivalent molecular geometry. The optimized molecular configuration is presented in Fig. 5a. The resulting molecule is called r–As₄S₃ in the study. The r–As₄S₃ molecule can be obtained from an initial model by which the S1 atom is removed from the pararealgar-type molecule (Fig. 3b): two paths lead to the r–As₄S₃ configuration in the As–S molecular hierarchy. The r–As₄S₃ comprises two types of trigonal pyramidal coordinations of an As atom; the As2 and As3 are bonded to two S atoms and one As atom, and the As1 and As4 are bonded to one S atom and two As atoms (Fig. 5a). The As–As bond lengths vary from 2.462 Å to 2.524 Å, but the As–S bonds differ very little from 2.241 Å to 2.270 Å (Table 3). The bond angles in the trigonal pyramid with two S atoms and one As atom are 84.7–98.59 °, whereas those with one S atom and two As atoms are widely distributed: 81.0–102.4°. The As1 and As4 including two As atoms in their coordination show lower atomic charges than As2 and As3 with only one As atom in the coordination (Table 4).

Second, an initial molecule model of an As_4S_3 was formed by removing the S3 from the pararealgar-type molecule (Fig. 3b). The optimized molecular configuration is presented in Fig. 5b. This is exactly the same molecule of dimorphite (Whitfield 1973a). The dimorphite-type molecule consists of two types of trigonal pyramidal coordinations; the As4 are bonded to three S atoms, and the As1, As2, and As3 are bonded to one S atom and two As atoms (Fig. 5b). The coordination of the As4 shows a perfectly symmetric trigonal pyramidal arrangement with As–S bond length of 2.236 Å and S–As–S bond angle of 99.07 ° (Table 3). The As4 with the symmetric trigonal pyramid lies on the three-fold rotation axis of an equilateral triangle geometry formed with As1–As2–As3. The As–S bond length in the trigonal pyramid of the As4 is approximately consistent with the measured values of 2.230 (8) and 2.234 (16) Å within experimental error (Whitfield 1973a). However, the As–S bond lengths of 2.236 Å in the trigonal pyramids of the As1, As2, and As3 are slightly longer than the measurement values ranging from 2.218 (10) to 2.221 (12) Å. The As–As bonds of 2.465 Å are, in contrast, slightly shorter than those ranging from 2.460 (7) to 2.480 (7). A large difference of 42.1 ° between the bond angles in the trigonal pyramid is observed in the coordinations of the As1, As2, and As3. The three As–S–As bond angles are 104.5 °, which shows good agreement with the observed values of 105.0 (4) and 105.4 (5) ° (Whitfield 1973a). The atomic charges of the As1, As2, and As3 which hold two As atoms in the coordination, are much lower than that of the As4 without As atoms in the coordination.

Third, an initial model for the structural optimization was formed by removing the S2 from the pararealgar-type molecule (Fig. 3b). The resulting molecular configuration is given in Fig. 5c. To date, As atom coordination environments of three types have been observed in arsenic sulfides. It is noteworthy that we can find a novel type of trigonal pyramidal coordinations of an As atom; the As1 is bonded to three As atoms (Fig. 5c). It is also noteworthy that the As1 carries a negative atomic charge of -0.029 (Table 4). The oxidation state of an As atom can be changed from -3 to +5 because the element arsenic has an electron configuration of $[\text{Ar}] 3d^{10}4s^24p^3$. Therefore, it is fully acceptable to consider that the As atom possesses a negative atomic charge in the molecule. In the study, the molecule is called p-As₄S₃. The p-As₄S₃ comprises trigonal pyramidal coordinations of two types: the As1 is bonded to three As atoms, and the As2, As3, As4 are bonded to one As atom and two S atoms. The As1 has an approximately symmetric trigonal pyramidal configuration with the As–As bond length of 2.490 Å and the As–As–As bond angle of 84.5 ° (Table 3). In trigonal pyramidal coordinations formed by the As2, As3, As4, the As–As, and the As–S bond lengths are 2.490 Å and 2.265 Å, respectively. The bond angles are, respectively, 89.15, 89.15, and 104.6 ° (Table 3). An estimated dipole moment of 2.509 D is consequently the highest value among the arsenic sulfide molecules (Table 4).

As₄S₂ molecules

First, a molecular model for an As₄S₂ was formed by removing S3 from the r-As₄S₃ molecule

(Fig. 5a). The optimized geometry with the bond lengths is given in Fig. 6a. The molecule consists of trigonal pyramidal As atom configurations of only one type; all As atoms are bonded to two As atoms and one S atom. The molecule is called r-As₄S₂. The trigonal pyramid has two As-As bonds of 2.492 Å and one As-S bond of 2.284 Å with bond angles of 75.6 and 87.7 °. The As-S bond length of 2.285 Å is the longest and the As-S-As bond angle of 84.0 ° is the smallest among all entire arsenic sulfide molecules examined in the study (Table 3). Atomic charges are equally distributed between four As atoms and two S atoms (Table 4). Furthermore, the r-As₄S₂ has the lowest dipole moment among those of all arsenic sulfide molecules.

A molecular model of an As₄S₂ was next formed by removing S5 from the dimorphite-type (Fig. 5b). The resulting optimized molecular configuration and its bond distances are shown in Fig. 6b. The molecule is called p-As₄S₂. The p-As₄S₂ was obtainable from initial models formed from both r-As₄S₃ and p-As₄S₃, as well. One model is formed by removal of the S1 from the r-As₄S₃ (Fig. 5a), and another by removing the S3 from the p-As₄S₃ (Fig. 5c): there are three paths leading to the p-As₄S₂ configuration in the As-S molecular hierarchy. The p-As₄S₂ includes an As atom forming the trigonal pyramid with three As atoms (Fig. 6b). In the coordination environment, As3 possesses a negative atomic charge of -0.028 (Table 4). The p-As₄S₂ comprises three types of trigonal pyramidal coordinations; the As4 is bonded to two S atoms and one As atoms, the As1 and As2 are bonded to one S atom and two As atoms, and the As3 is bonded to three As atoms. The As3 holds an

unsymmetrical trigonal pyramidal arrangement with two As–As bonds of 2.466 Å and one As–As bond of 2.510 Å because the As4 carries nearly twice as large a positive charge as that of the As1 and As2 (Table 4). Although the trigonal pyramid of the As3 is formed with four As atoms, the As–As bond angles vary widely from 60.3 to 81.7 °. A large difference of 42.2 ° between the bond angles is also observed in the trigonal pyramid of the As1, As2, and As4. The dipole moment of 1.699 D is approximately close to that of the pararealgar-type molecule.

As₄S molecule

An initial molecular model for an As₄S was formed by removing the S4 from the r–As₄S₂ molecule (Fig. 6a). The resulting optimized molecular configuration is presented in Fig. 7. The identical configuration was acquired from an initial model removing the S2 from the p–As₄S₂ (Fig. 6b). Therefore, two paths leading to the As₄S molecule configuration are in the As–S molecular hierarchy. The As₄S molecule contains trigonal pyramidal coordinations of an As atom of two types: the As2 and As4 are bonded to one S atom and two As atoms, and the As1 and As3 are bonded to three As atoms. Although the trigonal pyramids of the As1 and As3 are formed with four As atoms, they exhibit significantly distorted configurations consisting of one As–As bond of 2.4425 Å and two As–As bonds of 2.4565 Å (Table 3). The As–As–As bond angles are widely varied from 59.6 to 76.7 ° because the As1 and As3 with negative atomic charge are bonded to the As2 and As4 with positive atomic charge. The As–As bond of 2.443 Å is the shortest bond length among all As–As

bonds in all arsenic sulfide molecules. The As–S–As bond angle of 84.0° is also the smallest bond angle among all As–S–As bond angles in the study. In addition, the bond angle of 59.6° is the smallest among all bond angles in the study (Table 3). With decreasing S atom in arsenic molecules, an averaged atomic charge of As atoms approaches zero (Table 4). The dipole moment of the As_4S molecule is estimated as 1.488 D, which is nearly equivalent to that of ammonia 1.47 D (Nelson et al. 1967).

Structural diversity of arsenic sulfide molecules

Figure 8 shows the As–S molecular hierarchy diagram between As_4S_6 and As_4 . To date, molecular configurations of four types are known among the arsenic sulfide minerals (Bonazzi and Bindi, 2008). Although duranusite As_4S and dimorphite As_4S_3 have been known for many years, no mineral with a chemical formula between As_4S and As_4S_3 has been discovered. In the arsenic sulfide system, an additional six possible molecular configurations are predicted by ab initio quantum chemical investigation. The As_4S_6 molecule degrades to the As_4S_5 molecule directly, and the As_4S_5 molecule alternatively degrades to either realgar-type or pararealgar-type molecule. However, the molecular configurations are, structurally speaking, mutually incompatible. The molecular configuration of realgar goes down to the $r\text{-As}_4\text{S}_3$, whereas that of pararealgar engenders the three different molecular configurations of As_4S_3 . The $r\text{-As}_4\text{S}_3$ geometry is brought from both realgar and pararealgar. The $r\text{-As}_4\text{S}_3$ degrades to either $r\text{-As}_4\text{S}_2$ or $p\text{-As}_4\text{S}_2$ geometry, whereas both dimorphite

and the $p\text{-As}_4\text{S}_3$ degrade to $p\text{-As}_4\text{S}_2$. The $p\text{-As}_4\text{S}_2$ molecule therefore derives from three degradation pathways. An interesting result that might deserve special mention is that only one configuration is formed with three As atoms and one S atom, which strongly suggests that duranusite (Johan et al. 1973; Marquez-Zavalia et al., 1999; Mladenova, 2000) comprises the As_4S molecules (Fig. 7). Finally, a terminal molecule in the hierarchy is As_4 , which is experimentally observed as a yellow arsenic (e.g., Rodionov et al. 1979; Kalendarev et al. 1984; Rodionov et al. 1996; Kornath et al. 2009). Computed Raman spectroscopies of the entire molecules between As_4S_6 and As_4S are shown in Fig. 9. Raman spectroscopic analyses were performed to investigate the photoinduced alteration process from realgar to pararealgar (Muniz-Miranda et al. 1996). Profiles of the measured Raman spectra are apparently approximately consistent with those of the calculated spectra (Fig. 10). These spectral profiles simulated in the study can be helpful in the search for undiscovered arsenic sulfide minerals.

Similarly to an arsenic, a phosphorus belonging to group 15 in the periodic table usually possesses a pyramidal coordination geometry with a stereoactive lone pair. However, the P atom can have a tetrahedral coordination geometry with four S atoms as well because the lone pairs on the P atom are moved energetically to form stronger $\text{P}=\text{S}$ double bonds. A wide range of binary compounds is therefore known in the binary system of P and S. They comprise discrete cage-like molecules with the composition from P_4S_3 to P_4S_{10} (e.g., Von Schnering and Hönle, 1988; Jason et al.

1997). Although an As atom is also energetically capable of forming a tetrahedral coordination geometry with four S atoms, the tetrahedral coordination is exceedingly rare (e.g. Wood et al. 1996) and almost unknown. In arsenic sulfide polycations or polyanions, furthermore, cage-like molecular configurations of six types are known: $(\text{As}_2\text{S}_4)^{2-}$, $(\text{As}_2\text{S}_6)^{2-}$, $(\text{As}_3\text{S}_5)^+$, $(\text{As}_3\text{S}_6)^{2-}$, $(\text{As}_4\text{S}_6)^{2-}$, and $(\text{As}_{10}\text{S}_3)^{2-}$ (Porter and Sheldrick, 1971; Sheldrick and Kaub, 1985; Wendel and Muller, 1995; Smith et al. 1996). They also have cage-like molecular configurations. Therefore, the logical probability exists that arsenic sulfide minerals occur as molecular crystals with tetrahedral coordination or polycation/polyanion, but that probability seems extremely low.

ACKNOWLEDGMENTS

The author would like to thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of the paper. The work was supported by a Grant-in-Aid for Young Scientists (B) from the Japan Society for the Promotion of Science (project no. 24740352).

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FIGURE CAPTIONS

Figure 1 Optimized molecular geometry and the calculated bond length distribution of the As_4S_5 molecule.

Figure 2 Optimized As_4S_6 molecular geometry and its bond length distribution.

Figure 3 Optimized As_4S_4 molecular geometries and bond length distributions of (a) realgar-type and (b) pararealgar-type. The atomic labeling scheme corresponds to that of the As_4S_5 molecule in Fig. 1 because each molecule configuration is optimized from molecule models removing one S atom from the As_4S_5 molecule.

Figure 4 (a) Highest occupied molecular orbital (HOMO) and (b) the lowest unoccupied molecular orbital (LUMO) in As_4S_4 realgar-type molecule. The positive and negative phases are shown respectively as red and green.

Figure 5 Optimized As_4S_3 molecular geometries and their bond length distributions of (a) $r\text{-As}_4\text{S}_3$, (b) dimorphite-type, and (c) $p\text{-As}_4\text{S}_3$. The atomic labels of the $r\text{-As}_4\text{S}_3$ correspond to those of the realgar-type molecule in Fig. 3a. Those of the dimorphite-type and $p\text{-As}_4\text{S}_3$ correspond to those of the pararealgar-type molecule in Fig. 3b.

Figure 6 Optimized As_4S_2 molecular geometries and their bond length distributions of (a) $r\text{-As}_4\text{S}_2$ and (b) $p\text{-As}_4\text{S}_2$. The atomic labels of the $r\text{-As}_4\text{S}_2$ and $p\text{-As}_4\text{S}_2$ correspond respectively to those of the $r\text{-As}_4\text{S}_3$ (Fig. 5a) and dimorphite-type molecules (Fig. 5b).

Figure 7 Optimized As₄S molecular geometries and their bond length distributions. The atomic labels of the As₄S molecule correspond to those of both r-As₄S₂ and p-As₄S₂ (Fig. 6).

Figure 8 Structure hierarchy diagram of arsenic sulfide molecules from As₄S₆ to As₄S.

Figure 9 Simulated Raman spectra of arsenic sulfide molecules from As₄S₆ to As₄S.

Figure 10 Comparisons of Raman spectra between calculation and observation (Muniz-Miranda et al. 1996).

TABLE CAPTIONS

Table 1 Comparisons of bond lengths (Å) between observation and simulation

Table 2 Cartesian coordinates (Å) of the optimized molecular configurations

Table 3 Bond lengths (Å) and bond angles (°) in the optimized molecular configurations

Table 4 Atomic charge distributions, total energy (eV), and electric dipole moments (D) of the arsenic sulfide molecules

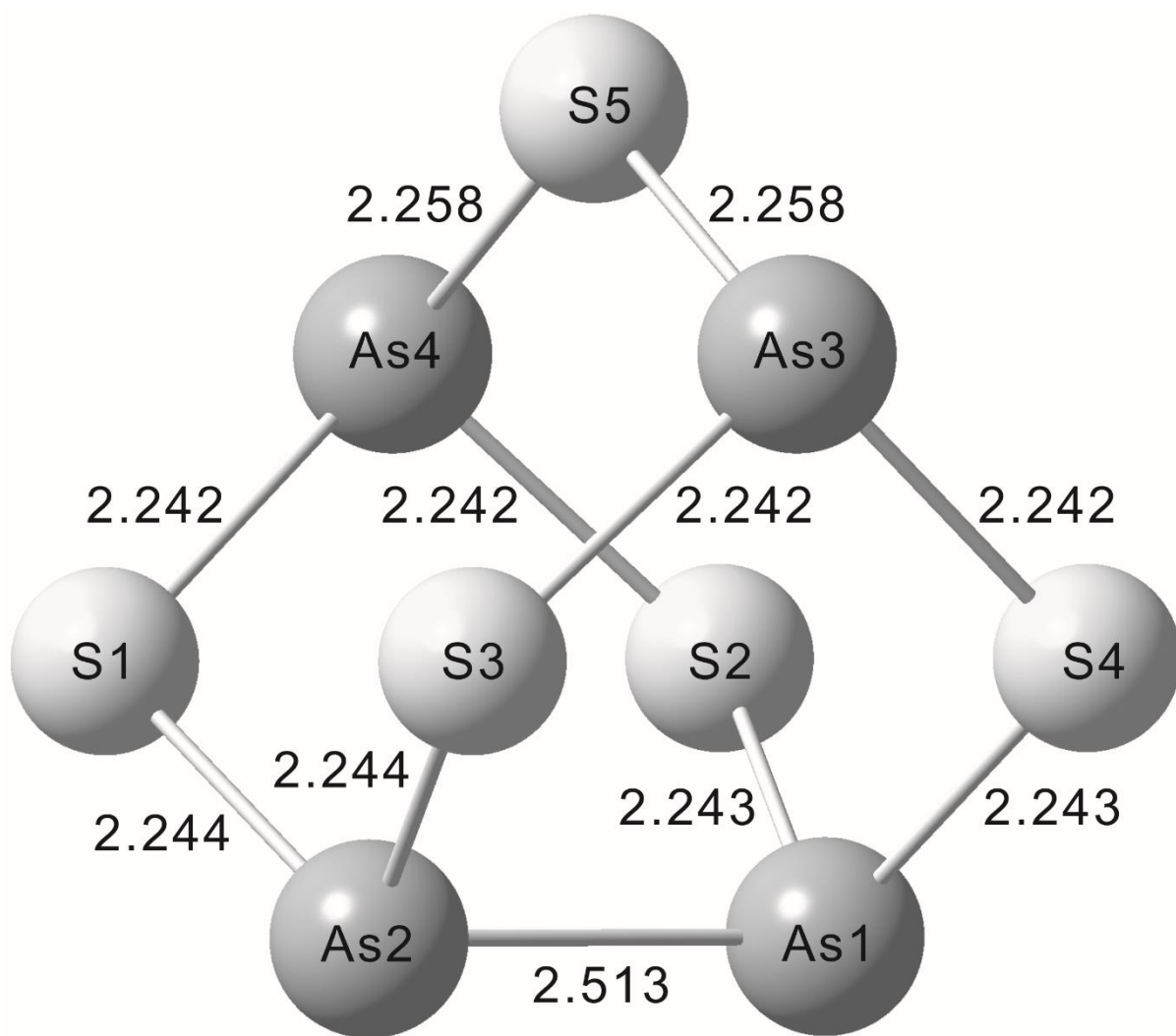


Figure 1

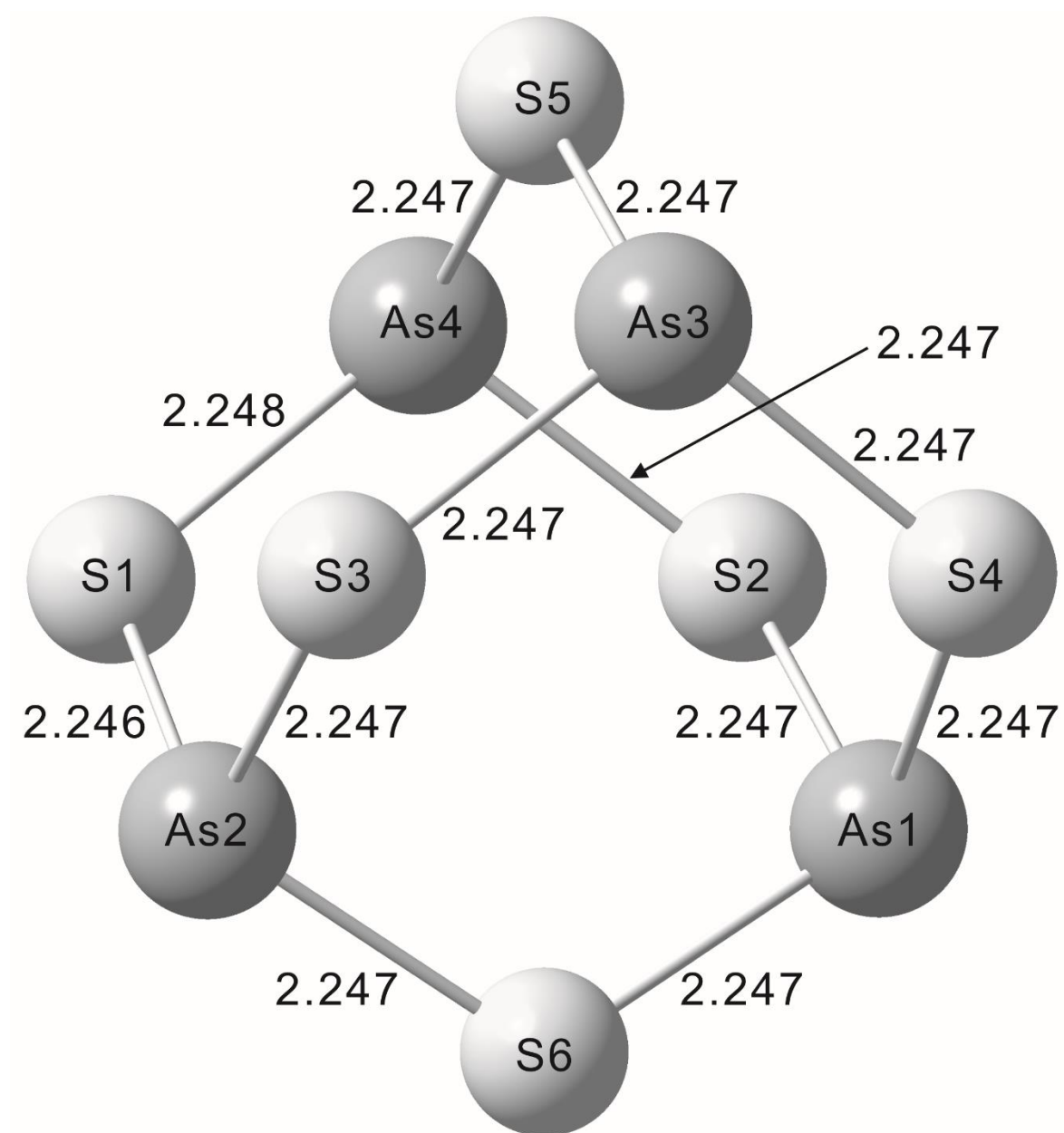


Figure 2

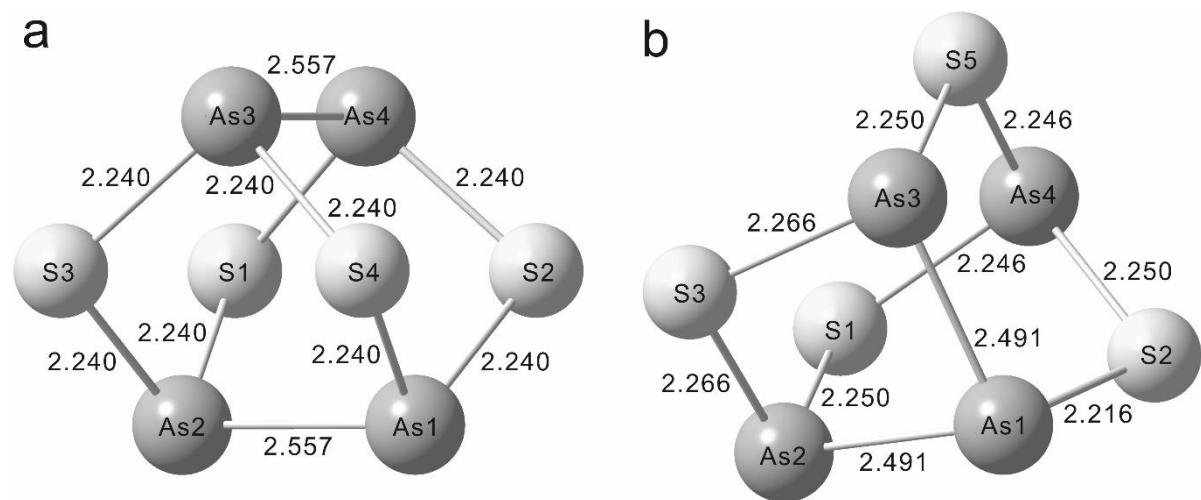


Figure 3

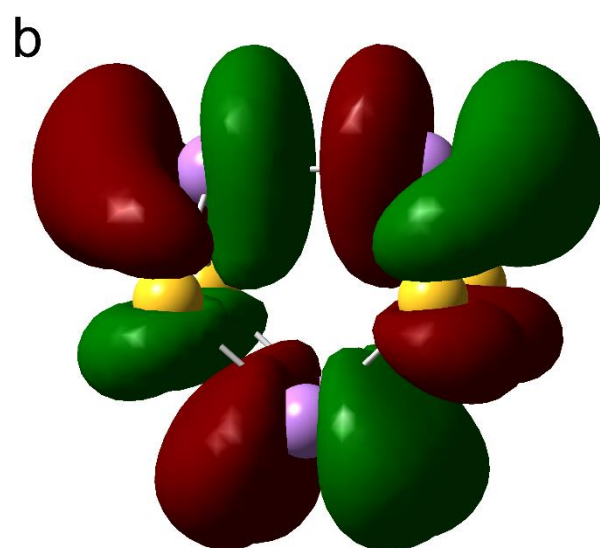
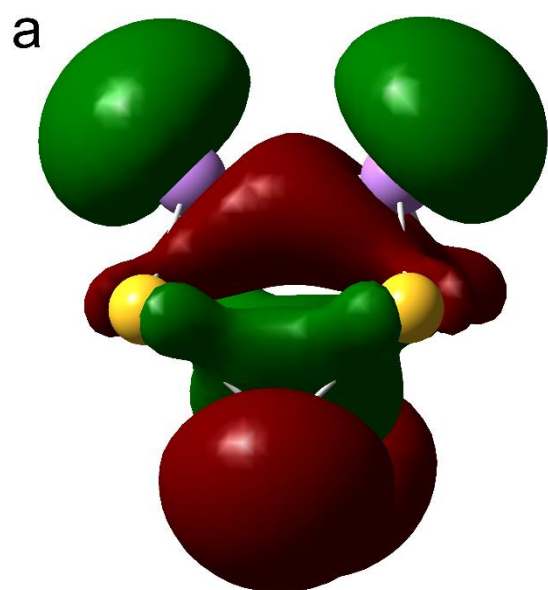


Figure 4

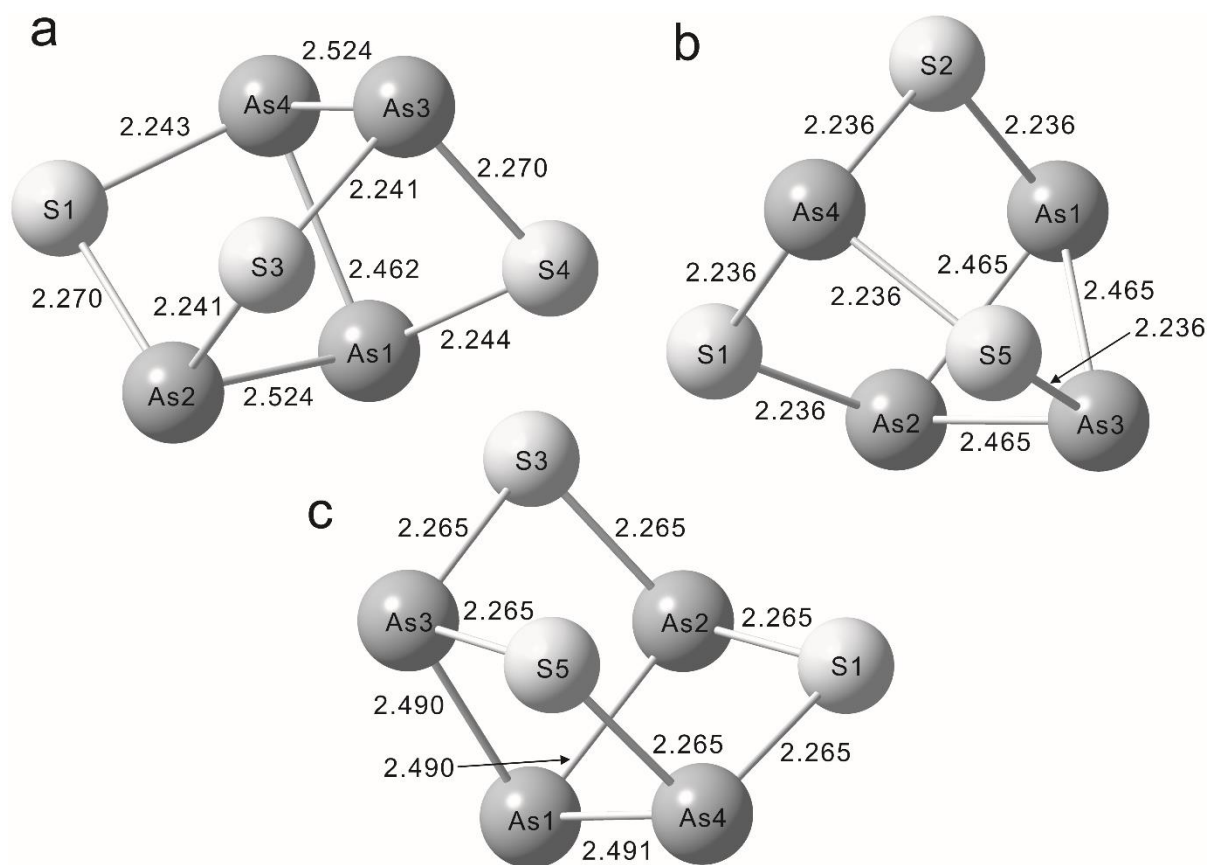


Figure 5

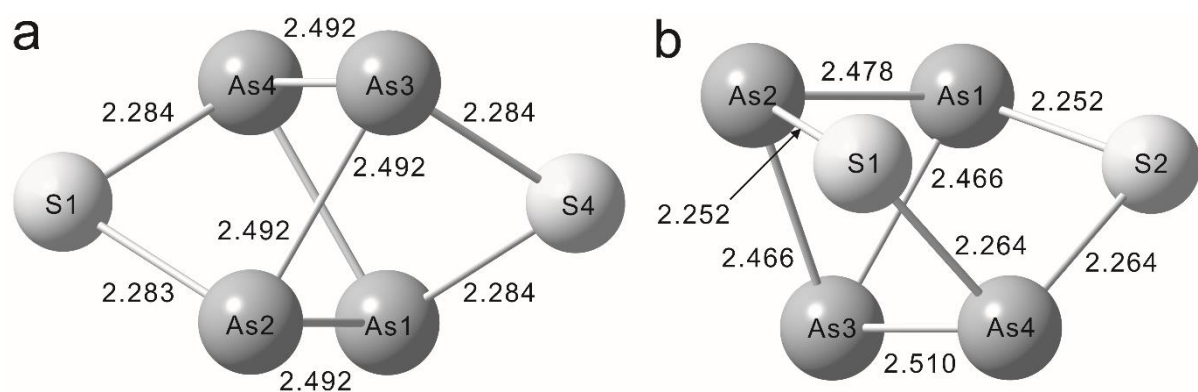


Figure 6

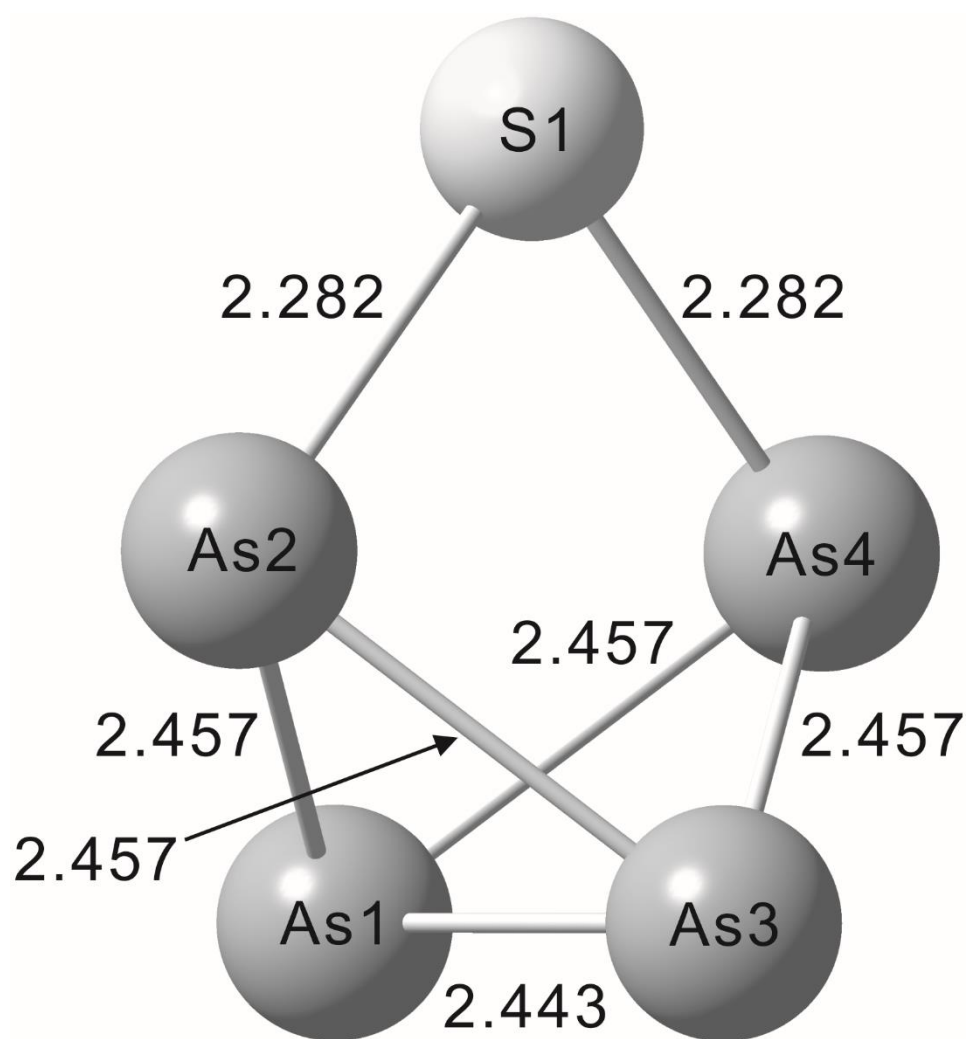


Figure 7

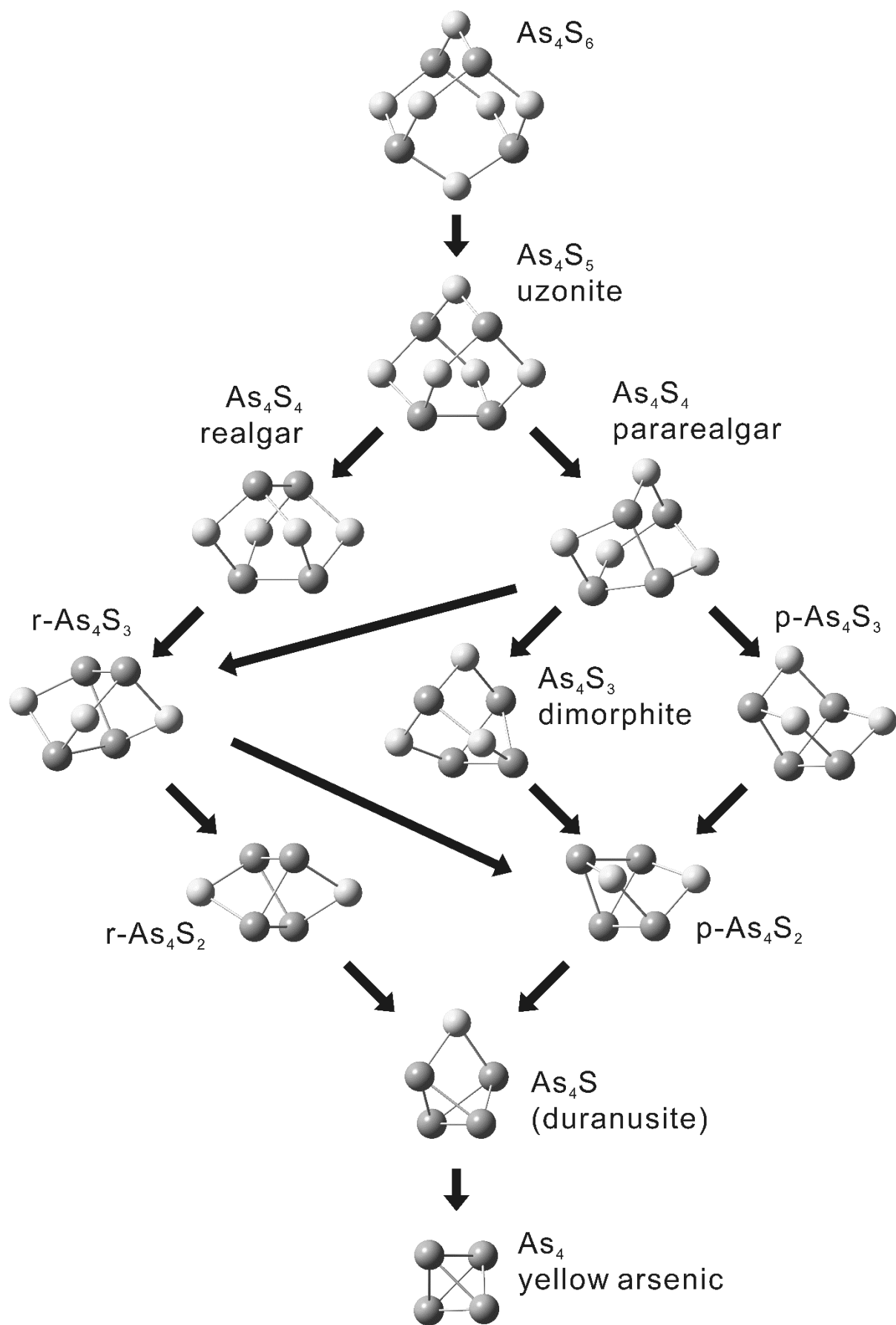


Figure 8

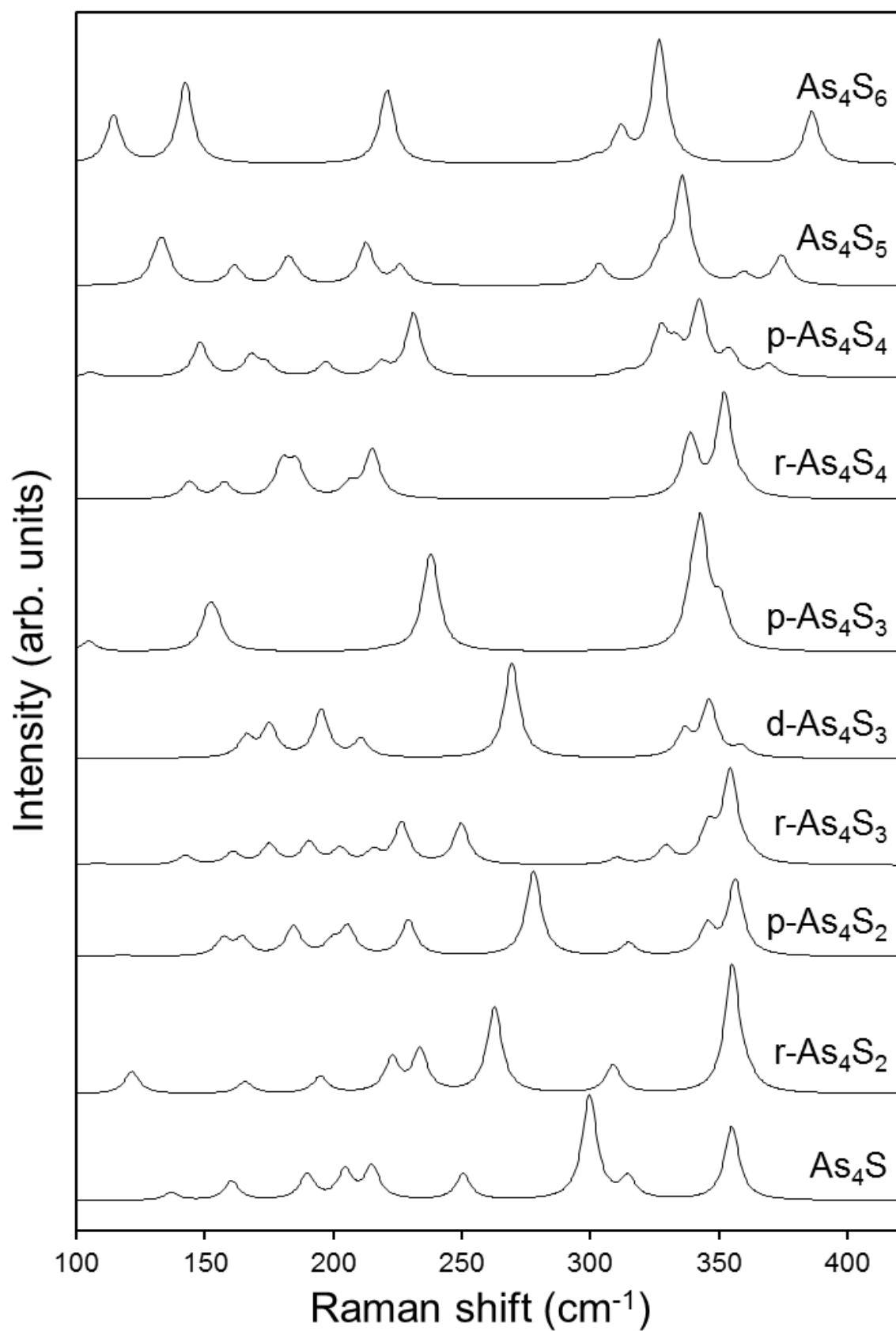


Figure 9

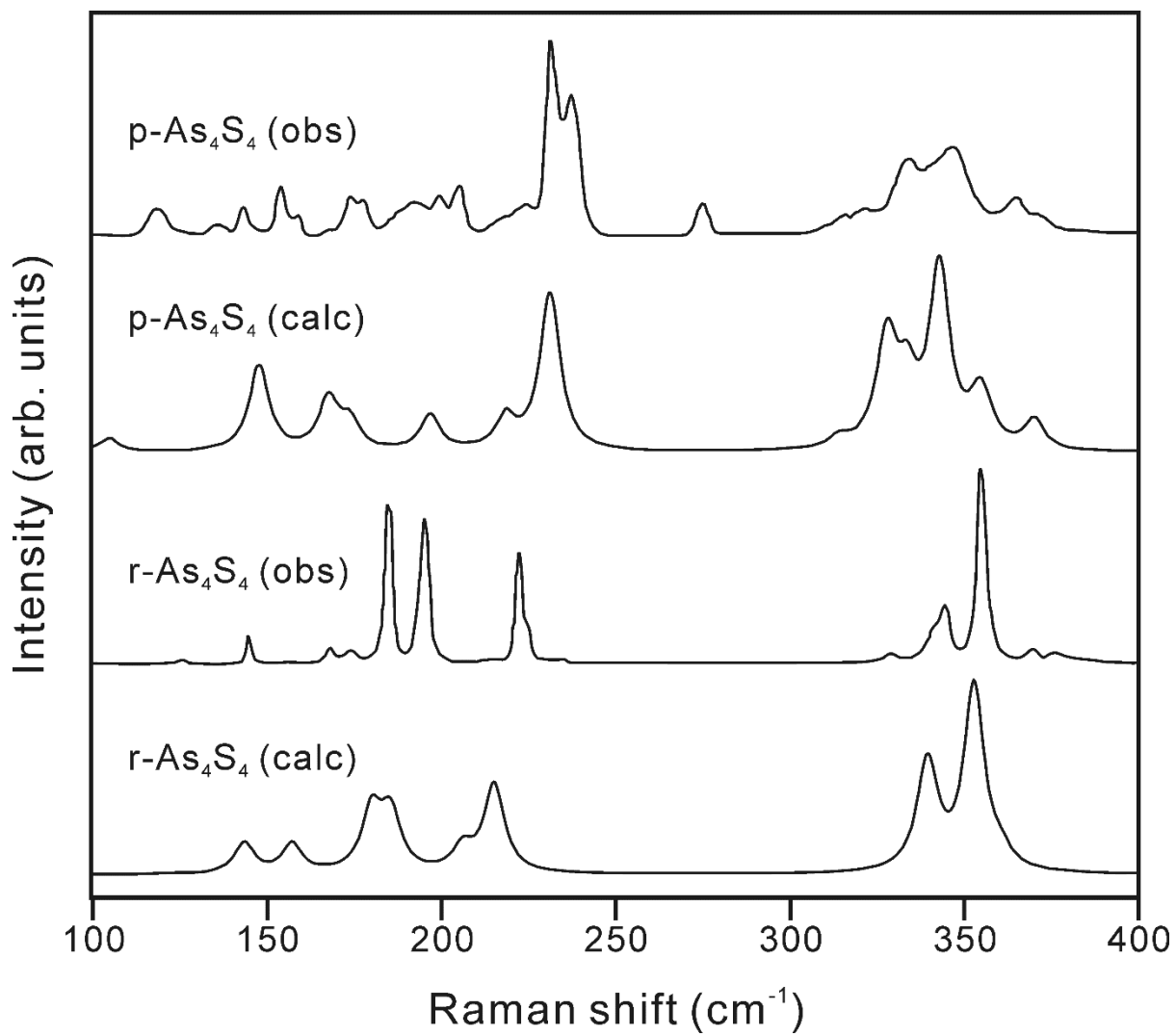


Figure 10

Table 1. Comparisons of bond length (\AA) between observation and simulation

| | | | Experimental measurement | B3LYP | | | | HF | | | | MP2 | | | |
|--|------|------------|-----------------------------|----------|-----------|-----------|------------|----------|-----------|-----------|------------|----------|-----------|-----------|------------|
| | | | | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) |
| As ₄ S ₃ dimorphite | | | | | | | | | | | | | | | |
| As1- | S1 | 2.230 (8) | 2.259 | 2.257 | 2.276 | 2.277 | 2.221 | 2.219 | 2.236 | 2.237 | 2.226 | 2.225 | 2.242 | 2.242 | |
| | S1' | 2.230 (8) | 2.259 | 2.257 | 2.276 | 2.277 | 2.221 | 2.219 | 2.236 | 2.237 | 2.226 | 2.225 | 2.242 | 2.242 | |
| | S2 | 2.234 (16) | 2.258 | 2.256 | 2.276 | 2.277 | 2.221 | 2.219 | 2.236 | 2.237 | 2.226 | 2.224 | 2.24 | 2.242 | |
| As2- | As3 | 2.460 (7) | 2.479 | 2.488 | 2.518 | 2.519 | 2.432 | 2.439 | 2.464 | 2.465 | 2.469 | 2.479 | 2.505 | 2.508 | |
| | As3' | 2.460 (7) | 2.479 | 2.488 | 2.518 | 2.519 | 2.432 | 2.439 | 2.464 | 2.465 | 2.469 | 2.479 | 2.505 | 2.508 | |
| | S2 | 2.221 (12) | 2.249 | 2.248 | 2.253 | 2.254 | 2.229 | 2.229 | 2.236 | 2.236 | 2.225 | 2.224 | 2.229 | 2.227 | |
| As3- | As3' | 2.480 (7) | 2.479 | 2.489 | 2.518 | 2.519 | 2.432 | 2.439 | 2.465 | 2.465 | 2.469 | 2.478 | 2.505 | 2.508 | |
| | S1 | 2.218 (10) | 2.249 | 2.247 | 2.253 | 2.253 | 2.229 | 2.228 | 2.236 | 2.236 | 2.225 | 2.223 | 2.228 | 2.227 | |
| As3'- | S1' | 2.218 (10) | 2.249 | 2.247 | 2.253 | 2.253 | 2.229 | 2.228 | 2.236 | 2.236 | 2.225 | 2.223 | 2.228 | 2.227 | |
| Δ | | | 0.023 | 0.025 | 0.043 | 0.044 | 0.018 | 0.016 | 0.010 | 0.010 | 0.007 | 0.008 | 0.019 | 0.020 | |
| As ₄ S ₄ realgar | | | | | | | | | | | | | | | |
| As1- | As4 | 2.570 (2) | 2.566 | 2.576 | 2.642 | 2.642 | 2.500 | 2.509 | 2.557 | 2.557 | 2.532 | 2.540 | 2.603 | 2.601 | |
| | S1 | 2.240 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| | S2 | 2.230 (5) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| As2- | As3 | 2.571 (2) | 2.568 | 2.577 | 2.643 | 2.642 | 2.501 | 2.510 | 2.557 | 2.557 | 2.532 | 2.540 | 2.602 | 2.601 | |
| | S1 | 2.248 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| | S3 | 2.247 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| As3- | S2 | 2.249 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| | S4 | 2.240 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| As4- | S3 | 2.232 (4) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| | S4 | 2.235 (5) | 2.257 | 2.260 | 2.270 | 2.270 | 2.227 | 2.230 | 2.240 | 2.241 | 2.230 | 2.233 | 2.241 | 2.242 | |
| Δ | | | 0.014 | 0.017 | 0.038 | 0.038 | 0.025 | 0.020 | 0.007 | 0.008 | 0.016 | 0.013 | 0.011 | 0.011 | |
| Note: Measurements of XRD analysis for dimorphite, realgar, pararealgar, and uzonite are reasured from Bindi et al. (2003), Kyono et al. (2005), Bonazzi et al. (1995), and Whitfield (1973a), respectively. Δ = Σ d _{exp} -d _{calc} /n | | | | | | | | | | | | | | | |

Table 1. ---Continued

| | | | B3LYP | | | | HF | | | | MP2 | | | |
|--|-----|------------|----------|-----------|-----------|------------|----------|-----------|-----------|------------|----------|-----------|-----------|------------|
| | | | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) | 6-31G(d) | 6-31+G(d) | 6-311G(d) | 6-311+G(d) |
| As ₄ S ₄ pararealgar | | | | | | | | | | | | | | |
| As1- | S1 | 2.254 (9) | 2.270 | 2.266 | 2.285 | 2.285 | 2.232 | 2.229 | 2.246 | 2.248 | 2.239 | 2.237 | 2.252 | 2.253 |
| | S3 | 2.238 (8) | 2.269 | 2.267 | 2.285 | 2.286 | 2.232 | 2.229 | 2.246 | 2.248 | 2.239 | 2.237 | 2.252 | 2.253 |
| | S4 | 2.261 (8) | 2.278 | 2.279 | 2.299 | 2.299 | 2.234 | 2.235 | 2.250 | 2.251 | 2.246 | 2.247 | 2.264 | 2.264 |
| As2- | As4 | 2.484 (4) | 2.496 | 2.503 | 2.553 | 2.553 | 2.445 | 2.452 | 2.491 | 2.490 | 2.475 | 2.482 | 2.529 | 2.528 |
| | S1 | 2.251 (9) | 2.268 | 2.268 | 2.279 | 2.280 | 2.239 | 2.239 | 2.250 | 2.251 | 2.239 | 2.239 | 2.247 | 2.247 |
| | S2 | 2.252 (9) | 2.297 | 2.299 | 2.305 | 2.306 | 2.257 | 2.259 | 2.266 | 2.267 | 2.271 | 2.273 | 2.277 | 2.278 |
| As3- | As4 | 2.534 (4) | 2.496 | 2.503 | 2.554 | 2.553 | 2.445 | 2.452 | 2.491 | 2.490 | 2.475 | 2.482 | 2.529 | 2.528 |
| | S2 | 2.244 (10) | 2.296 | 2.299 | 2.306 | 2.307 | 2.257 | 2.259 | 2.266 | 2.267 | 2.271 | 2.273 | 2.277 | 2.278 |
| | S3 | 2.228 (10) | 2.269 | 2.268 | 2.279 | 2.279 | 2.239 | 2.239 | 2.250 | 2.251 | 2.239 | 2.239 | 2.247 | 2.247 |
| As4- | S4 | 2.190 (9) | 2.223 | 2.228 | 2.229 | 2.230 | 2.204 | 2.209 | 2.216 | 2.216 | 2.198 | 2.203 | 2.203 | 2.204 |
| Δ | | | 0.030 | 0.031 | 0.044 | 0.044 | 0.024 | 0.024 | 0.016 | 0.016 | 0.018 | 0.017 | 0.016 | 0.044 |
| As ₄ S ₅ uzonite | | | | | | | | | | | | | | |
| As1- | As2 | 2.527 (1) | 2.526 | 2.535 | 2.594 | 2.594 | 2.465 | 2.472 | 2.513 | 2.513 | 2.492 | 2.501 | 2.551 | 2.549 |
| | S1 | 2.240 (1) | 2.261 | 2.264 | 2.273 | 2.273 | 2.231 | 2.234 | 2.243 | 2.244 | 2.236 | 2.239 | 2.245 | 2.246 |
| | S1' | 2.240 (1) | 2.261 | 2.264 | 2.273 | 2.273 | 2.231 | 2.234 | 2.243 | 2.244 | 2.236 | 2.239 | 2.245 | 2.246 |
| As2- | S2 | 2.249 (1) | 2.260 | 2.264 | 2.272 | 2.273 | 2.231 | 2.234 | 2.244 | 2.244 | 2.236 | 2.239 | 2.245 | 2.245 |
| | S2' | 2.249 (1) | 2.260 | 2.264 | 2.272 | 2.273 | 2.231 | 2.234 | 2.244 | 2.244 | 2.236 | 2.239 | 2.245 | 2.245 |
| As3- | S1 | 2.237 (1) | 2.267 | 2.266 | 2.285 | 2.285 | 2.227 | 2.227 | 2.242 | 2.243 | 2.236 | 2.236 | 2.251 | 2.251 |
| | S2 | 2.251 (1) | 2.267 | 2.266 | 2.285 | 2.285 | 2.227 | 2.227 | 2.242 | 2.244 | 2.236 | 2.236 | 2.251 | 2.252 |
| | S3 | 2.261 (1) | 2.278 | 2.275 | 2.297 | 2.297 | 2.241 | 2.238 | 2.258 | 2.258 | 2.247 | 2.245 | 2.263 | 2.262 |
| As3'- | S1' | 2.237 (1) | 2.267 | 2.266 | 2.285 | 2.285 | 2.227 | 2.227 | 2.242 | 2.243 | 2.236 | 2.236 | 2.251 | 2.251 |
| | S2' | 2.251 (1) | 2.267 | 2.266 | 2.285 | 2.285 | 2.227 | 2.227 | 2.242 | 2.244 | 2.236 | 2.236 | 2.251 | 2.252 |
| | S3 | 2.261 (1) | 2.278 | 2.275 | 2.297 | 2.297 | 2.241 | 2.238 | 2.258 | 2.258 | 2.247 | 2.245 | 2.263 | 2.262 |
| Δ | | | 0.017 | 0.018 | 0.038 | 0.038 | 0.020 | 0.019 | 0.006 | 0.006 | 0.012 | 0.010 | 0.007 | 0.007 |

Note: Measurements of XRD analysis for dimorphite, realgar, pararealgar, and uzonite are referead from Bindi et al. (2003), Kyono et al. (2005), Bonazzi et al. (1995), and Whitfield (1973a), respectively. $\Delta = \Sigma |d_{\text{exp}} - d_{\text{calc}}| / n$

Table 2. Cartesian coordinates (Å) of the optimized molecular configurations

| <i>x</i> <i>y</i> <i>z</i> | | | <i>x</i> <i>y</i> <i>z</i> | | | <i>x</i> <i>y</i> <i>z</i> | | |
|--|----------|----------|--|-----|----------|--------------------------------------|----------|--------------------------------|
| As₄S₆ | | | As₄S₅ | | | | | |
| As1 | -1.45765 | -1.82588 | -0.03339 | As1 | -1.56738 | -1.25689 | 0.00000 | |
| As2 | 1.42133 | -0.10361 | -1.85137 | As2 | -1.56770 | 1.25649 | 0.00000 | |
| As3 | -1.23398 | 1.98270 | -0.07476 | As3 | 1.21981 | 0.00018 | 1.92995 | |
| As4 | 1.27084 | -0.05338 | 1.95991 | As4 | 1.21981 | 0.00018 | -1.92995 | |
| S1 | 2.53061 | -0.14690 | 0.10106 | S1 | -0.23918 | 1.69370 | -1.75431 | |
| S2 | -0.17573 | -1.76655 | 1.81112 | S2 | -0.23918 | -1.69355 | -1.75449 | |
| S3 | 0.17526 | 1.76628 | -1.81142 | S3 | -0.23918 | 1.69370 | 1.75431 | |
| S4 | -2.53079 | 0.14746 | -0.10157 | S4 | -0.23918 | -1.69355 | 1.75449 | |
| S5 | 0.03432 | 1.81365 | 1.77239 | S5 | 2.39109 | -0.00021 | 0.00000 | |
| S6 | -0.03478 | -1.81358 | -1.77238 | | | | | |
| As₄S₄-realgar | | | As₄S₄-pararealgar | | | | | |
| As1 | 1.09628 | -0.97039 | 1.27848 | As1 | -0.67270 | -0.00048 | 1.61893 | |
| As2 | 1.09628 | -0.97039 | -1.27848 | As2 | -1.07381 | -1.67502 | -0.18046 | |
| As3 | -1.94398 | 0.01301 | 0.00000 | As3 | -1.07322 | 1.67549 | -0.17959 | |
| As4 | -0.24887 | 1.92802 | 0.00000 | As4 | 2.15942 | -0.00010 | -0.40924 | |
| S1 | 1.09628 | 1.23822 | -1.65335 | S1 | 0.97266 | -1.77409 | -1.10998 | |
| S2 | 1.09628 | 1.23822 | 1.65335 | S2 | 1.53871 | -0.00100 | 1.75362 | |
| S3 | -1.09600 | -1.23847 | -1.65335 | S3 | -2.12291 | 0.00073 | -1.28712 | |
| S4 | -1.09600 | -1.23847 | 1.65335 | S5 | 0.97344 | 1.77456 | -1.10892 | |
| r-As₄S₃ | | | As₄S₃-dimorphite | | | p-As₄S₃ | | |
| As1 | 0.14150 | -1.19383 | -1.22120 | As1 | 1.17193 | 1.42136 | -0.06646 | As1 -0.00002 -0.00009 1.56294 |
| As2 | 1.60473 | 0.78478 | -0.65828 | As2 | 1.17182 | -0.76829 | -1.19771 | As2 1.41146 -1.32166 -0.00658 |
| As3 | -1.60468 | 0.78715 | 0.65605 | As3 | 1.17180 | -0.65316 | 1.26418 | As3 -1.85032 -0.56154 -0.00655 |
| As4 | -0.14129 | -1.18946 | 1.22455 | As4 | -2.06525 | 0.00007 | -0.00001 | As4 0.43874 1.88320 -0.00649 |
| S1 | 1.89907 | -0.26346 | 1.33382 | S1 | -0.99711 | -1.06054 | -1.65348 | S1 1.97985 0.60092 -1.06089 |
| S3 | -0.00017 | 2.20551 | -0.00400 | S2 | -0.99702 | 1.96223 | -0.09173 | S3 -0.46947 -2.01460 -1.06111 |
| S4 | -1.89943 | -0.26862 | -1.33212 | S5 | -0.99711 | -0.90166 | 1.74521 | S5 -1.51009 1.41387 -1.06109 |

Table 2. --Continued

| <i>x</i> <i>y</i> <i>z</i> | | | <i>x</i> <i>y</i> <i>z</i> | | | <i>x</i> <i>y</i> <i>z</i> | | |
|--------------------------------------|----------|----------|--------------------------------------|----------|----------|----------------------------|----------|----------|
| r-As₄S₂ | | | p-As₄S₂ | | | As₄S | | |
| As1 | 0.62058 | -1.10845 | As1 | -0.71020 | -1.01524 | As1 | -1.00969 | -0.00004 |
| As2 | -0.62059 | -1.05161 | As2 | -0.71020 | -1.01524 | As2 | 0.48104 | 1.52330 |
| As3 | 0.62064 | 1.10847 | As3 | 1.40704 | -0.76451 | As3 | -1.00967 | -0.00001 |
| As4 | -0.62063 | 1.05164 | As4 | 0.70204 | 1.64440 | As4 | 0.48112 | -1.52328 |
| S1 | -2.31760 | -0.00005 | S1 | -0.71020 | 1.18654 | S1 | 2.18048 | 0.00005 |
| S4 | 2.31760 | -0.00007 | S2 | -0.71020 | 1.18654 | | | -0.00001 |

Table 3. Bond lengths (Å) and bond angles (°) in the optimized molecular configurations

| bond lengths | | | bond angles | | bond lengths | | | bond angles | |
|--|--------|----------------|-------------|--|--------------|-----------------|--------|-------------|--|
| As₄S₆ | | | | As₄S₅ | | | | | |
| As1 - S2 | 2.2470 | S2 - As1 - S4 | 105.91 | As1 - As2 | 2.5134 | As2 - As1 - S2 | 101.23 | | |
| - S4 | 2.2473 | As1 - S6 | 105.90 | - S2 | 2.2436 | As1 - S4 | 101.23 | | |
| - S6 | 2.2470 | S4 - As1 - S6 | 105.91 | - S4 | 2.2436 | S2 - As1 - S4 | 102.87 | | |
| As2 - S1 | 2.2460 | S1 - As2 - S3 | 105.93 | As2 - As1 | 2.5134 | As1 - As2 - S1 | 101.23 | | |
| - S3 | 2.2474 | As2 - S6 | 105.95 | - S1 | 2.2434 | As2 - S3 | 101.23 | | |
| - S6 | 2.2473 | S3 - As2 - S6 | 105.86 | - S3 | 2.2434 | S1 - As2 - S3 | 102.90 | | |
| As3 - S3 | 2.2470 | S3 - As3 - S4 | 105.90 | As3 - S3 | 2.2424 | S3 - As3 - S4 | 98.11 | | |
| - S4 | 2.2473 | As3 - S5 | 105.91 | - S4 | 2.2422 | As3 - S5 | 105.70 | | |
| - S5 | 2.2470 | S4 - As3 - S5 | 105.91 | - S5 | 2.2576 | S4 - As3 - S5 | 105.71 | | |
| As4 - S1 | 2.2475 | S1 - As4 - S2 | 105.92 | As4 - S1 | 2.2424 | S1 - As4 - S2 | 98.11 | | |
| - S2 | 2.2472 | As4 - S5 | 105.90 | - S2 | 2.2422 | As4 - S5 | 105.70 | | |
| - S5 | 2.2472 | S2 - As4 - S5 | 105.88 | - S5 | 2.2576 | S2 - As4 - S5 | 105.71 | | |
| | | As2 - S1 - As4 | 116.19 | | | As2 - S1 - As4 | 107.42 | | |
| | | As1 - S2 - As4 | 116.21 | | | As1 - S2 - As4 | 107.42 | | |
| | | As2 - S3 - As3 | 116.21 | | | As2 - S3 - As3 | 107.42 | | |
| | | As1 - S4 - As3 | 116.18 | | | As1 - S4 - As3 | 107.42 | | |
| | | As3 - S5 - As4 | 116.21 | | | As3 - S5 - As4 | 117.50 | | |
| | | As1 - S6 - As2 | 116.21 | | | | | | |
| As₄S₄-realgar | | | | As₄S₄-pararealgar | | | | | |
| As1 - As2 | 2.5570 | As2 - As1 - S2 | 99.63 | As1 - As2 | 2.4905 | As2 - As1 - As3 | 84.54 | | |
| - S2 | 2.2402 | As1 - S4 | 99.63 | - As3 | 2.4908 | As1 - S2 | 101.80 | | |
| - S4 | 2.2402 | S2 - As1 - S4 | 95.16 | - S2 | 2.2155 | As3 - As1 - S2 | 101.80 | | |
| As2 - As1 | 2.5570 | As1 - As2 - S1 | 99.63 | As2 - As1 | 2.4905 | As1 - As2 - S1 | 100.46 | | |
| - S1 | 2.2402 | As2 - S3 | 99.63 | - S1 | 2.2499 | As2 - S3 | 86.00 | | |
| - S3 | 2.2402 | S1 - As2 - S3 | 95.16 | - S2 | 2.2657 | S1 - As2 - S3 | 104.59 | | |
| As3 - As4 | 2.5574 | As4 - As3 - S3 | 99.64 | As3 - As1 | 2.4908 | As1 - As3 - S3 | 85.99 | | |
| - S3 | 2.2403 | As3 - S4 | 99.64 | - S3 | 2.2657 | As3 - S5 | 100.46 | | |
| - S4 | 2.2403 | S3 - As3 - S4 | 95.12 | - S5 | 2.2500 | S3 - As3 - S5 | 104.60 | | |
| As4 - As3 | 2.5574 | As3 - As4 - S1 | 99.64 | As4 - S1 | 2.2464 | S1 - As4 - S2 | 98.85 | | |
| - S1 | 2.2403 | As4 - S2 | 99.64 | - S2 | 2.2502 | As4 - S5 | 104.35 | | |
| - S2 | 2.2403 | S1 - As4 - S2 | 95.12 | - S5 | 2.2462 | S2 - As4 - S5 | 98.86 | | |
| | | As2 - S1 - As4 | 100.37 | | | As2 - S1 - As4 | 108.47 | | |
| | | As1 - S2 - As4 | 100.37 | | | As1 - S2 - As4 | 102.53 | | |
| | | As2 - S3 - As3 | 100.37 | | | As2 - S3 - As3 | 95.36 | | |
| | | As1 - S4 - As3 | 100.37 | | | As3 - S5 - As4 | 108.47 | | |

Table 3. --Continued

| bond lengths | | | bond angles | | bond lengths | | bond angles | |
|--|--------|-----------------|-------------|--|--------------|-----------------|-------------|--|
| α -As ₄ S ₃ | | | | As ₄ S ₃ -dimorphite | | | | |
| As1 - As2 | 2.5244 | As2 - As1 - As4 | 81.01 | As1 - As2 | 2.4646 | As2 - As1 - As3 | 60.00 | |
| - As4 | 2.4621 | As1 - S4 | 102.42 | - As3 | 2.4646 | As1 - S2 | 102.11 | |
| - S4 | 2.2436 | As4 - As1 - S4 | 86.78 | - S2 | 2.2355 | As3 - As1 - S2 | 102.11 | |
| As2 - As1 | 2.5244 | As1 - As2 - S1 | 84.77 | As2 - As1 | 2.4646 | As1 - As2 - As3 | 60.00 | |
| - S1 | 2.2702 | As2 - S3 | 98.45 | - As3 | 2.4646 | As2 - S1 | 102.11 | |
| - S3 | 2.2410 | S1 - As2 - S3 | 97.43 | - S1 | 2.2355 | As3 - As2 - S1 | 102.11 | |
| As3 - As4 | 2.5242 | As4 - As3 - S3 | 98.45 | As3 - As1 | 2.4646 | As1 - As3 - As2 | 60.00 | |
| - S3 | 2.2410 | As3 - S4 | 84.74 | - As2 | 2.4646 | As3 - S5 | 102.11 | |
| - S4 | 2.2703 | S3 - As3 - S4 | 97.43 | - S5 | 2.2355 | As2 - As3 - S5 | 102.11 | |
| As4 - As1 | 2.4621 | As1 - As4 - As3 | 81.04 | As4 - S1 | 2.2360 | S1 - As4 - S2 | 99.07 | |
| - As3 | 2.5242 | As4 - S1 | 86.83 | - S2 | 2.2360 | As4 - S5 | 99.07 | |
| - S1 | 2.2433 | As3 - As4 - S1 | 102.42 | - S5 | 2.2360 | S2 - As4 - S5 | 99.07 | |
| | | As2 - S1 - As4 | 91.72 | | | As2 - S1 - As4 | 104.52 | |
| | | As2 - S3 - As3 | 101.39 | | | As1 - S2 - As4 | 104.52 | |
| | | As1 - S4 - As3 | 91.74 | | | As3 - S5 - As4 | 104.52 | |
| β -As ₄ S ₃ | | | | α -As ₄ S ₂ | | | | |
| As1 - As2 | 2.4904 | As2 - As1 - As3 | 84.51 | As1 - As2 | 2.4919 | As2 - As1 - As4 | 75.64 | |
| - As3 | 2.4904 | As1 - As4 | 84.51 | - As4 | 2.4920 | As1 - S4 | 87.70 | |
| - As4 | 2.4905 | As3 - As1 - As4 | 84.50 | - S4 | 2.2835 | As4 - As1 - S4 | 87.70 | |
| As2 - As1 | 2.4904 | As1 - As2 - S1 | 89.15 | As2 - As1 | 2.4919 | As1 - As2 - As3 | 75.64 | |
| - S1 | 2.2652 | As2 - S3 | 89.15 | - As3 | 2.4920 | As2 - S1 | 87.70 | |
| - S3 | 2.2650 | S1 - As2 - S3 | 104.56 | - S1 | 2.2834 | As3 - As2 - S1 | 87.70 | |
| As3 - As1 | 2.4904 | As1 - As3 - S3 | 89.15 | As3 - As2 | 2.4920 | As2 - As3 - As4 | 75.63 | |
| - S3 | 2.2650 | As3 - S5 | 89.15 | - As4 | 2.4919 | As3 - S4 | 87.70 | |
| - S5 | 2.2650 | S3 - As3 - S5 | 104.55 | - S4 | 2.2835 | As4 - As3 - S4 | 87.70 | |
| As4 - As1 | 2.4905 | As1 - As4 - S1 | 89.15 | As4 - As1 | 2.4920 | As1 - As4 - As3 | 75.63 | |
| - S1 | 2.2652 | As4 - S5 | 89.15 | - As3 | 2.4919 | As4 - S1 | 87.70 | |
| - S5 | 2.2650 | S1 - As4 - S5 | 104.56 | - S1 | 2.2835 | As3 - As4 - S1 | 87.70 | |
| | | As2 - S1 - As4 | 95.34 | | | As2 - S1 - As4 | 84.00 | |
| | | As2 - S3 - As3 | 95.35 | | | As1 - S4 - As3 | 84.00 | |
| | | As3 - S5 - As4 | 95.35 | | | | | |

Table 3. --Continued

| bond lengths | | | | bond angles | | bond lengths | | | | bond angles | |
|---|--------|-----------------|--------|-------------------|--------|-----------------|-------|--|--|-------------|--|
| β -As ₄ S ₂ | | | | As ₄ S | | | | | | | |
| As1 - As2 | 2.4780 | As2 - As1 - As3 | 59.84 | As1 - As2 | 2.4565 | As2 - As1 - As3 | 60.19 | | | | |
| - As3 | 2.4659 | As1 - S2 | 102.06 | - As3 | 2.4425 | As1 - As4 | 76.65 | | | | |
| - S2 | 2.2515 | As3 - As1 - S2 | 90.32 | - As4 | 2.4565 | As3 - As1 - As4 | 60.19 | | | | |
| As2 - As1 | 2.4780 | As1 - As2 - As3 | 59.84 | As2 - As1 | 2.4565 | As1 - As2 - As3 | 59.62 | | | | |
| - As3 | 2.4659 | As2 - S1 | 102.06 | - As3 | 2.4565 | As2 - S1 | 92.18 | | | | |
| - S1 | 2.2515 | As3 - As2 - S1 | 90.32 | - S1 | 2.2822 | As3 - As2 - S1 | 92.18 | | | | |
| As3 - As1 | 2.4659 | As1 - As3 - As2 | 60.32 | As3 - As1 | 2.4425 | As1 - As3 - As2 | 60.19 | | | | |
| - As2 | 2.4659 | As3 - As4 | 81.74 | - As2 | 2.4565 | As3 - As4 | 60.19 | | | | |
| - As4 | 2.5100 | As2 - As3 - As4 | 81.74 | - As4 | 2.4565 | As2 - As3 - As4 | 76.65 | | | | |
| As4 - As3 | 2.5100 | As3 - As4 - S1 | 88.92 | As4 - As1 | 2.4565 | As1 - As4 - As3 | 59.62 | | | | |
| - S1 | 2.2642 | As4 - S2 | 88.92 | - As3 | 2.4565 | As4 - S1 | 92.18 | | | | |
| - S2 | 2.2642 | S1 - As4 - S2 | 98.06 | - S1 | 2.2822 | As3 - As4 - S1 | 92.18 | | | | |
| | | As2 - S1 - As4 | 92.29 | | | As2 - S1 - As4 | 84.00 | | | | |
| | | As1 - S2 - As4 | 92.29 | | | | | | | | |
| | | | | | | | | | | | |
| bond lengths | | Min | Max | Δ | | | | | | | |
| As - As | | 2.4425 | 2.5574 | 0.1149 | | | | | | | |
| As - S | | 2.2155 | 2.2835 | 0.0680 | | | | | | | |
| | | | | | | | | | | | |
| bond angles | | Min | Max | Δ | | | | | | | |
| As - As - As | | 59.62 | 84.54 | 24.92 | | | | | | | |
| As - As - S | | 88.92 | 101.23 | 12.31 | | | | | | | |
| As - S - As | | 84.00 | 117.50 | 33.50 | | | | | | | |
| S - As - S | | 97.43 | 105.95 | 8.52 | | | | | | | |

Table 4. Atomic charge distributions, total energy (eV), and electric dipole moments (D) of the arsenic sulfide molecules

| | As ₄ S ₆ | As ₄ S ₅ | As ₄ S ₄ | | As ₄ S ₃ | | | As ₄ S ₂ | | As ₄ S |
|----------------|--------------------------------|--------------------------------|--------------------------------|---------------|--------------------------------|---------------|---------------|--------------------------------|---------------|-------------------|
| | | | realgar | pararealgar | α | dimorphite | β | α | β | |
| As1 | 0.213 | 0.131 | 0.126 | 0.071 | 0.092 | 0.070 | -0.029 | 0.101 | 0.088 | -0.025 |
| As2 | 0.213 | 0.131 | 0.126 | 0.159 | 0.143 | 0.070 | 0.179 | 0.101 | 0.088 | 0.120 |
| As3 | 0.212 | 0.217 | 0.126 | 0.159 | 0.143 | 0.070 | 0.179 | 0.101 | -0.028 | -0.025 |
| As4 | 0.213 | 0.217 | 0.126 | 0.213 | 0.092 | 0.194 | 0.179 | 0.101 | 0.161 | 0.120 |
| Average | 0.213 | 0.174 | 0.126 | 0.150 | 0.117 | 0.101 | 0.127 | 0.101 | 0.077 | 0.048 |
| S1 | -0.142 | -0.135 | -0.126 | -0.153 | -0.158 | -0.135 | -0.169 | -0.201 | -0.154 | -0.191 |
| S2 | -0.142 | -0.135 | -0.126 | -0.131 | | -0.135 | | | -0.154 | |
| S3 | -0.142 | -0.135 | -0.126 | -0.164 | -0.153 | | -0.169 | | | |
| S4 | -0.142 | -0.135 | -0.126 | | -0.158 | | | -0.201 | | |
| S5 | -0.141 | -0.159 | | -0.153 | | -0.135 | -0.169 | | | |
| S6 | -0.142 | | | | | | | | | |
| Average | -0.142 | -0.140 | -0.126 | -0.150 | -0.156 | -0.135 | -0.169 | -0.201 | -0.154 | -0.191 |
| Total energy | -307959 | -297146 | -286333 | -286333 | -275519 | -275519 | -275518 | -264705 | -264705 | -253891 |
| Dipole moment | 0.007 | 0.953 | 0.002 | 1.605 | 1.160 | 1.270 | 2.509 | 0.000 | 1.699 | 1.488 |